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SOME ASPECTS OF ELECTROWINNING OF LEAD FOR TREATMENT OF SCRAP LEAD ACID BATTERIES

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Disposal of lead acid batteries has assumed importance with constant growth of automobile industries. Paste fraction of the battery waste is always an area of environmental concern. Pyrometallurgical operation currently employed causes emission of oxides of lead and particulate lead causing atmospheric pollution. Electrolytic route is investigated as an alternative. Anodic deposition of PbO_2 is a major problem identified in the electrowinning of lead. Addition of certain soluble compounds of phosphorous or arsenic is found to inhibit PbO_2 effectively. Levelling of lead deposit is another aspect of investigation. Addition of levelling agent and grain refiner in proper proportion avoids dendritic growth. Over potential measurement is found to be useful in monitoring the concentration of additives in the electrolyte during electrowinning of lead.

Keywords: Recovery of lead, scrap batteries and electrowinning.

INTRODUCTION

Lead production from the secondary lead industry represents a substantial portion of the lead produced. The annual production of automobile batteries is 4 million units from which 40,000 tonnes of lead can be recovered. Pyro-metallugical route currently practiced suffers from environmental problems like emission of lead particulates and oxides of sulphur [1-4]. This problem can be avoided in the electrolytic route which offers lead of high purity suitable for maintenance free batteries and oxides.

The deposition of lead oxide on the anode during the electrowinning of lead is a major problem and should be minimised. Appropriate remedial measures like addition of certain soluble compounds of phosphorous and arsenic to inhibit PbO_2 deposition have been investigated in this paper.

Another aspect which assumes importance is the levelling of lead deposit is another problem studied. Addition of levelling agent and grain refiner in proper concentration avoids dendritic growth. The concentration of additives in the lead electrowinning electrolyte has been monitored by measurements of over potential.

EXPERIMENTAL

Lead fluoborate electrolyte containing 60 $g.l^{-1}$ lead and 150 $g.l^{-1}$ free fluoboric acid was taken in a cell made up of PVC of capacity 500 ml. A lead sheet and platinum gauze were employed as cathode and anode respectively. Arsenic as arsenic trioxide was added to the electrolyte in the concentration range of 100 to 4000 ppm. A current density of 200 Am^{-2} was employed and the amount of lead dioxide formed on the anode was estimated. The experiment was repeated with different amounts of phosphorous as phosphoric acid and cobalt as cobalt nitrate added separately to the electrolyte.

Cathode overpotential measurements were made in a solution containing 60 $g.l^{-1}$ and 150 $g.l^{-1}$ fluoboric acid and 4 $g.l^{-1}$ sodium lignin sulphonate using a thin lead sheet and a pure lead foil of area 2 cm^2 each as anode and cathode respectively. A lead reference electrode was employed for these measurements. Current density ranging from 100 to 800 Am^{-2} was applied using a galvanostat and the corresponding cathode overpotential was measured using a lead reference electrode. Amount of gelatin was varied from 50 to 3000 ppm and the corresponding polarisation data was measured. The experiment was repeated with addition of 50 to 3000 ppm of glue to the

electrolyte and also polarisation data were measured at different temperatures for the varying amount of gelatin.

RESULTS AND DISCUSSION

In the electrowinning operation, the anodic deposition of lead dioxide is found to result in the loss of lead from the electrolyte.

The anodic reaction is

$$Pb(BF_4)_2 + 2H_2O = PbO_2 + 2H^+ + 2HBF_4 + 2e \quad (1)$$

The cathodic reaction is

$$Pb(BF_4)_2 + 2H^+ + 2e = Pb + 2HBF_4 \quad (2)$$

The overall reaction is

$$Pb(BF_4)_2 + 2H_2 = PbO_2 + Pb + 4HBF_4 \quad (3)$$

In essence, one mole of lead at the cathode generates one mole of PbO_2 at the anode. In this context, some remedial measures like addition of certain inorganic compounds like arsenic, phosphorous and cobalt were investigated [5]. Fig. 1 shows the effect of these compounds on deposition of lead dioxide. Among the three species namely cobalt, arsenic and phosphorous, arsenic was found to be more effective and the level of arsenic addition was found to be 2000 ppm where the current efficiency for PbO_2 formation drops from 100% to less than 1%. This may be due to that when arsenic is present in the electrolyte in small amounts, oxygen over potential is reduced [6]. The result is that O_2 evolution is promoted inhibiting PbO_2 formation at the anode.

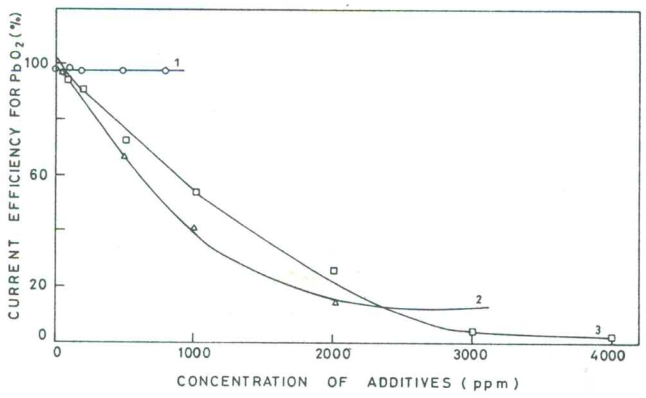

Fig. 1: Effect of electrolyte additives on PbO_2 formation on platinum in lead fluoborate solution of 50 g.l^{-1} Pb, 150 g.l^{-1} fluoboric acid, 4 g.l^{-1} goulac and 2 g.l^{-1} gelatin at 400 A.m^{-2} (1) Co (2) As (3) P

Role of addition agents

In the electrodeposition of lead, tree growth and needle shaped formations are very common. Some additives like lignin sulphonate (goulac) as grain refiner and gelatin or glue as levelling agent are added to get a fine grained smooth lead deposits. Fig. 2 shows the polarisation curves for electrodeposition of lead from lead electrolyte containing 50 g.l^{-1} lead, 150 g.l^{-1} fluoboric acid, 4 g.l^{-1} goulac with additions of gelatin ranging from 0 to 3000 ppm keeping the concentration of goulac at constant level of 4 g.l^{-1}. The nearly linear polarisation/current density relationship suggests that the addition agents form a voltage barrier at the cathode surface due to adsorption of additives on to the plating surface, resulting in the rise of cathode potential. The cathode over potential rises to 150 mV when gelatin is present at 2000 ppm when compared to a potential value of 50 mV when there is no addition agents present at a current density of 2000 A.m^{-2}. In

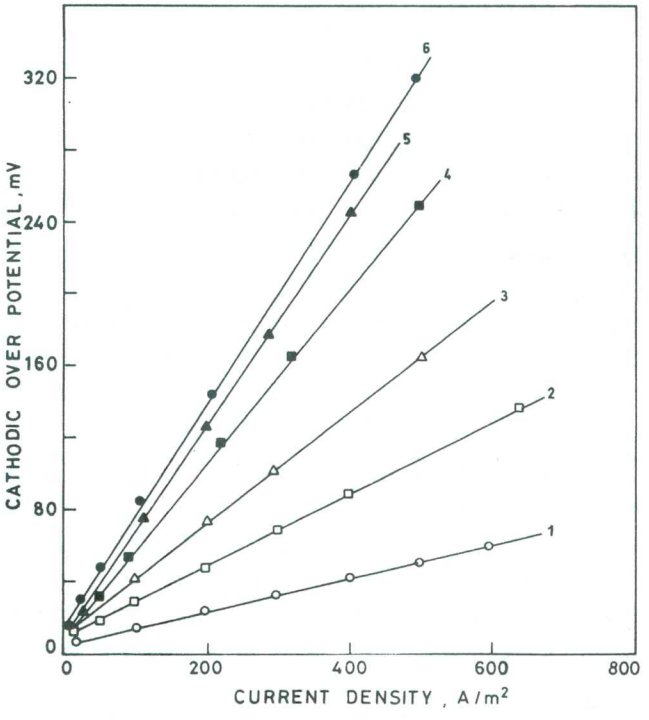

Fig. 2: Galvanostatic polarisation curves for electro deposition of Pb from lead fluoborate soluion containing 50 g.l^{-1} Pb, 150 g.l^{-1} fluoboric acid and 4 g.l^{-1} goulac with additions of gelatin (1) 0 ppm (2) 100 ppm (3) 500 ppm (4) 1000 ppm (5) 2000 ppm (6) 3000 ppm

other words, a 50 mV rise is not large enough to cause uniform current density on all parts of cathode surface but a 150 mV rise, does produce the required levelling action.

The slope of the polarisation curve for the addition of 500 ppm of gelatin is found to be 0.3 mV $A^{-1}.m^2$ and this glue increases to 0.6 mV $A^{-1}.m^2$ for the gelatin concentration of 2000 ppm.

It is reported [7] that an excellent polarisation curve refers to an approximately linear polarisation curve with a slope of 0.43 mV $A^{-1}.m^2$ at 400 $A.m^{-2}$ and very good polarisation curve is approximately linear with a slope of 0.43 mV $A^{-1}.m^2$ at 200 $A.m^{-2}$ and a good polarisation curve refers to non linear polarisation curve giving approximately 85 mV at 200 $A.m^{-2}$, a fair polarisation curve is non linear passing between 40 and 60 mV at 200 $A.m^{-2}$ and a poor polarisation curve gives less than 30 mV upto 400 $A.m^{-2}$.

Fig. 3 shows the over potential time curves for electrodeposition of lead from a solution containing 50 to 100 $g.l^{-1}$ lead, 150 $g.l^{-1}$ fluoboric acid, 4 $g.l^{-1}$ goulac and 2 $g.l^{-1}$ gelatin. When deposition is carried out for long duration the polarisation of lead is found to decrease indicating the consumption of gelatin with time. When polarisation measurements were made, degradation of additives takes place linearly as function of time during the couple of hours. It is reported [8] in the case of copper electrorefining that gelatin is decomposed after 12 hrs.

Polarisation caused by addition of 2 $g.l^{-1}$ gelatin in a solution containing 50 $g.l^{-1}$ lead, 150 $g.l^{-1}$ fluoboric acid and 4 $g.l^{-1}$ goulac is also studied at different temperatures and is shown in Fig. 4. When the temperature increases polarisation of cathode lead decreases.

The effect of agitation on cathode polarisation in a solution containing 50 $g.l^{-1}$ lead, 150 $g.l^{-1}$ fluoboric acid, 4 $g.l^{-1}$ goulac and 2 $g.l^{-1}$ gelatin is shown in Fig. 5. The cathode polarisation decreases with increasing agitation which indicates that the addition agent barrier at the plating surface is not a tightly adsorbed film. The function of lignin sulphonate is to provide a suspension of colloidal particles on which the levelling agent and the lead complex are absorbed and dispersed throughout the diffusion layer next to the cathode [9]. This function facilitates levelling of deposit by the levelling agent. Lignin sulfonate acts as a grain refiner i.e. decreases the crystal size by blocking the growth of individual crystals resulting

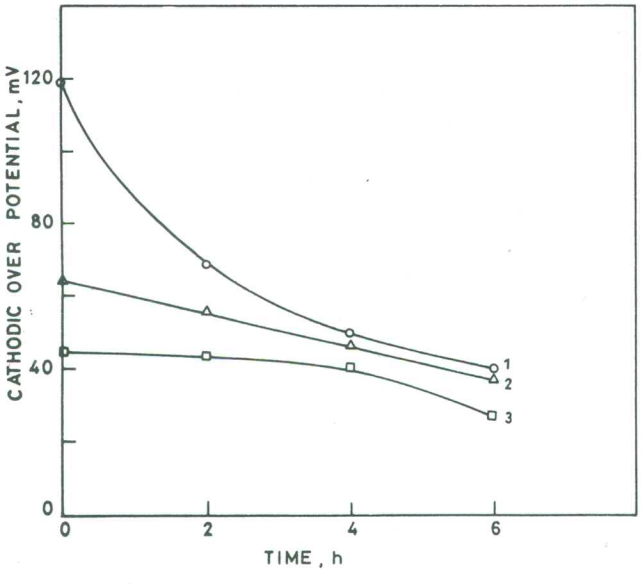

Fig. 3: Cathodic overpotential time curves for electrodeposition of Pb from lead fluoborate solutions with additions of 4 $g.l^{-1}$ goulac and 2 $g.l^{-1}$ gelatin at 400 $A.m^{-2}$ at different lead ion concentration (1) 50 $g.l^{-1}$ (2) 70 $g.l^{-1}$ (3) 100 $g.l^{-1}$

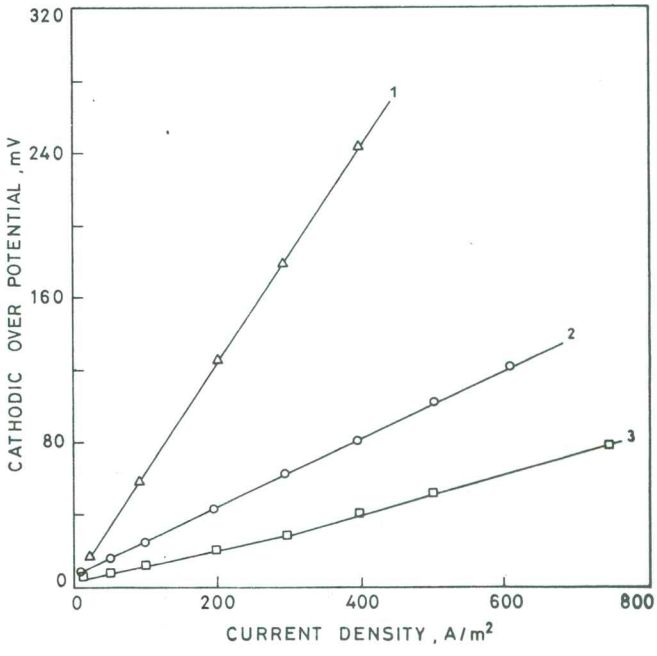

Fig. 4: Galvanostatic polarisation curves for electrodeposition of Pb from lead fluoborate solution containing 50 $g.l^{-1}$ Pb, 150 $g.l^{-1}$ fluoboric acid, 4 $g.l^{-1}$ goulac and 2 $g.l^{-1}$ gelatin at different temperatures (1) 303 K (2) 313 K (3) 333 K

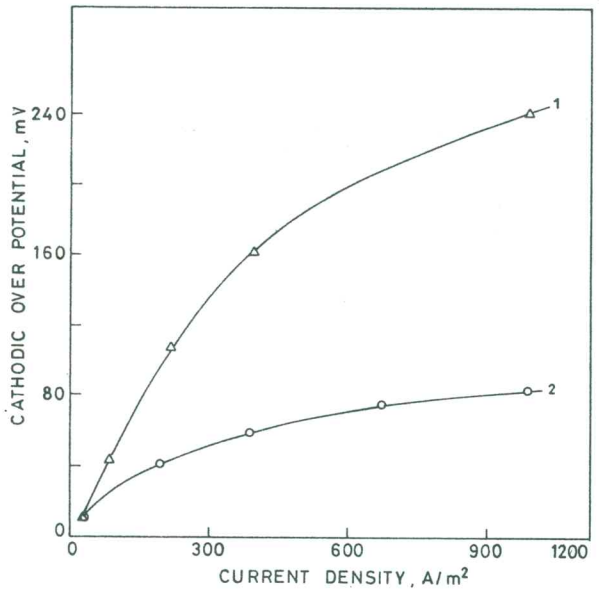

Fig. 5: Galvanostatic polarisation curve for electrodeposition of lead form lead fluoborate solutions containing 50 g.l^{-1} Pb, 150 g.l^{-1} fluoboric acid 4 g.l^{-1} goulac and 2 g.l^{-1} of gelatin under (1) stirring (2) stationary conditions

in a greatly increased nucleation rate for lead crystallites.

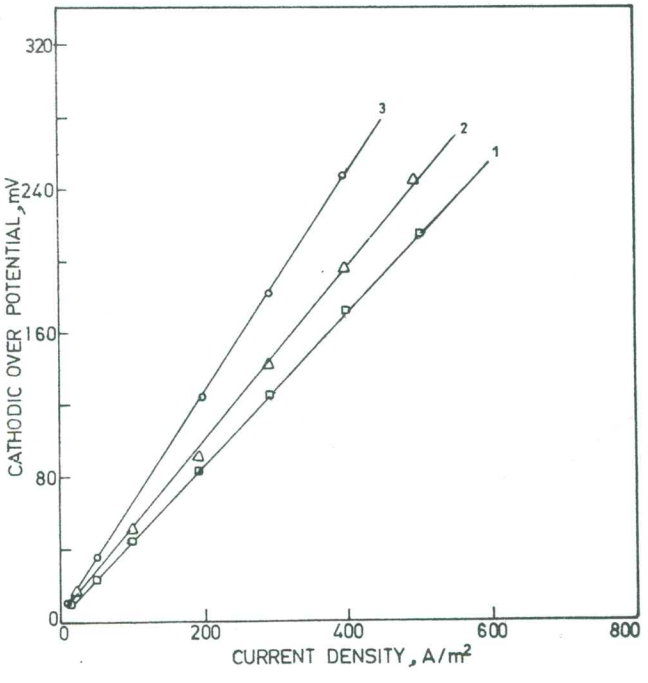

Fig. 6: Effect of levelling agent, on the polarisation for electro deposition of lead from lead fluoborate solution containing 50 g.l^{-1} lead, 150 g.l^{-1} fluoboric acid and 4 g.l^{-1} goulac with (1) fish flue (2) animal glue (3) gelatin

Fig. 6 shows the polarisation curves for three different addition agents viz. gelatin, animal glue and fish glue and among the three, gelatin was found to be more effective.

The adsorption of gelatin decreases the amount of free and active sites and often acts as inhibitors. They adsorb on the cathode surface where they involve in the electrochemical deposition of lead. These additives restrict the growth of existing crystals and force the deposition to take place via the formation of new nuclei. The organic additive is adsorbed selectively on the active growth site and drive the natural growth direction to alter. It is also possible that the additives react with lead ion forming a complex in the cathode film and in such a case effect the local polarisation process [7].

CONCLUSION

- In the electrowinning of lead, addition of arsenic or phosphorous compounds to the electrolyte is found to inhibit formation of PbO_2 at the anode.
- Addition of gelatin is found to polarise the cathode to the extent of 80 to 100 mV improving the physical nature of lead deposit. This phenomenon is found useful in monitoring the concentration of additives in the electrolyte during electrowinning of lead.

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